

A Mechanism of Bismuth Orthovanadate Structure Formation during Solvothermal Synthesis

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Abstract—Using solvothermal synthesis, we have prepared bismuth orthovanadate samples suitable as pigments for the lacquer and paint coating industry. We have determined their elemental and phase compositions and unit-cell parameters. The bismuth orthovanadate structure formation mechanism has been studied in the course of solvothermal synthesis. The physicochemical characteristics of the samples obtained (particle size, true density, oil absorption, and pH of aqueous suspension) have been investigated.

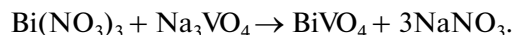
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INTRODUCTION

In a number of countries, lead and chromium compounds are used as yellow anticorrosion pigments in the lacquer and paint coating industry. However, because of the ever more stringent requirements for environmental security, the use of such pigments is limited, and there is an intensive search for alternative, less toxic pigments. Dyckerhoff [1] considered the possibility of replacing toxic yellow pigments containing lead and chromium compounds by bismuth orthovanadate, an environmentally safe compound that has a higher coloring power and purer hue. At present, vanadates are commonly synthesized by high-temperature and hydrochemical processes [2, 3]. As a rule, the sintering of metal oxides, carbonates, or nitrates with V_2O_5 or NH_4VO_3 requires much energy and leads to the formation of impurity phases, such as compounds of vanadium in lower oxidation states, and toxic gaseous by-products. A more attractive approach to the preparation of bismuth orthovanadate is solvothermal synthesis with the use of aqueous electrolyte solutions as precursors [4]. This process allows one to control the properties of the resulting dispersed phase by varying synthesis conditions (the nature and concentration of reactants and solvents, solution pH, temperature, reaction sequence, and others), is easy to implement, can be run at atmospheric pressure and relatively low temperatures (under 100°C), and needs no special apparatus. The formation of a precipitate in solution involves the nucleation, growth, and aggregation of crystals and recrystallization through the solution or coalescence of the crystals. In each of these steps, the particle size and purity can be controlled by selecting appropriate conditions [5].

EXPERIMENTAL

Bismuth orthovanadate was prepared by solvothermal synthesis using an alkaline solution of sodium orthovanadate ($\text{pH} \approx 13$) and an acid solution of bismuth nitrate ($\text{pH} \approx 0$) as precursors:



The starting chemicals used were reagent-grade NaVO_3 and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Bismuth nitrate and sodium metavanadate were dissolved in 1 N solutions of nitric acid and sodium hydroxide, respectively.

The NaVO_3 dissolution in the alkali leads to the formation of sodium orthovanadate [6]. The dissolution ensured a uniform distribution of the starting chemicals over the entire solution, a high degree of dispersion, high diffusion rate of the reactants, and, hence, a high reaction rate even at room temperature.

Bismuth orthovanadate synthesis included the following steps:

- (1) mixing of the alkaline sodium vanadate solution with the acid bismuth salt solution in the molar ratio $\text{Bi} : \text{V} = 1 : 1$;
- (2) adjustment of the resultant mixture to $\text{pH} 3.5$ by adding a 30% sodium hydroxide solution;
- (3) stirring for 1 h at room temperature;
- (4) gradual addition of a 1 N sodium hydroxide solution and adjustment of the mixture to $\text{pH} 6$ over a period of 1 h;
- (5) heating of the mixture and holding at the boiling point and $\text{pH} \approx 6$ for 3 h (pH was adjusted by a 1 N sodium hydroxide solution);
- (6) cooling of the mixture to room temperature, filtration, and washing of the precipitate with distilled water; and
- (7) drying of the precipitate at 90°C .

Table 1. Particle size distributions in powder samples *1–6*

Particle size, μm	Percentage					
	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>
0.1–1	0	4.37	3.34	0	0	0
1–2	0	3.14	1.13	0	0.02	0
2–3	0	9.72	0.04	0	1.43	3.55
3–4	0	1.74	0	0	2.43	14.72
4–5	0.11	0.03	0	0	3.76	12.56
5–10	40.33	2.29	3.64	0.13	42.99	23.94
10–20	40.61	16.99	17.46	24.70	25.09	45.23
20–50	0.37	61.72	54.92	74.76	24.28	0
50–100	0	0	19.47	0.41	0	0
100–200	0	0	0	0	0	0
200–600	18.58	0	0	0	0	0
Total size range, μm	4–600	0.2–40	0.1–90	9–60	2–50	2–11

In steps 1–4, we took samples which were numbered in the same way as the corresponding steps in the bismuth orthovanadate synthesis (*1–4*). In step 5, after the mixture was held at its boiling point for 1.5 and 3 h, we took samples 5 and 6, respectively.

The morphology and elemental composition of the synthesis products were assessed by scanning electron microscopy on a JEOL JSM-5610 LV equipped with an EDX JED-2201 energy dispersive X-ray microanalysis system, which ensured an accuracy of 0.5% or better.

The phase composition of the synthesis products was determined by X-ray diffraction on a D8 Advance AXS diffractometer (Bruker, Germany) with $\text{CuK}\alpha$ radiation. X-ray diffraction data were analyzed using the EVA program, incorporated into the DiffractPlus software package supplied with the diffractometer. The phases present were identified using Powder Diffraction File data.

The particle size of the pigments was determined with an Analysette 22 laser particle sizer (measurement range 0.1–602.5 μm).

The true density was determined by the Archimedes method in conformity with the RF State Standard GOST 21229.5. The oil absorption value of

the pigments and the pH of an aqueous 10% suspension were determined by standard procedures (RF State Standards GOST 21229.8 and GOST 21229.3, respectively).

RESULTS AND DISCUSSION

In the first step of synthesis, the addition of small amounts of a sodium orthovanadate solution to the bismuth salt leads to the formation of a bright yellow colloidal solution. First, the forming crystalline nuclei are small because particles of the disperse phase are in a suspended state for a rather long time. On further addition of the precipitant to a Bi : V molar ratio of 1 : 1 in solution, the precipitation of a large number of minute nuclei continues. The material precipitates from the supersaturated solution predominantly on the surface of the nuclei. This leads to the formation of relatively large particles in the precipitate. Sample *1* contains a phase (18.58%) with a particle size in the range 200–600 μm (Table 1). The particle size of the major phase (>80%) is 5–20 μm . According to scanning electron microscopy data (Fig. 1), the particles have a nearly cylindrical shape, with a branched base.

EDX microanalysis data indicate that the V : Bi molar ratio in the synthesis product (sample *1*) is 1.15 : 1.0 (Table 2), which can be interpreted as evidence that the sample contains trace amounts of V_2O_5 and bismuth meta- and polyvanadates. According to X-ray diffraction data (Fig. 2), the sample is single-phase and has the bismuth orthovanadate structure [7], which is indirect evidence that the impurity phases in the synthesis product are X-ray amorphous.

The degree of ion condensation depends on the solution pH and total vanadium concentration in solution. It is known that the maximum degree of condensation is observed in acid media [8]. X-ray diffraction data demonstrate that, during ripening of the product in solutions with $\text{pH} < 1$, the precipitated bismuth orthovanadate contains solid decavanadate

Table 2. Elemental composition of bismuth orthovanadate samples

Sample	Weight percent		V : Bi molar ratio
	V	Bi	
<i>1</i>	21.84	78.16	1.15 : 1
<i>2</i>	15.41	71.53	0.88 : 1
<i>3</i>	16.38	64.34	1.04 : 1
<i>4</i>	17.17	77.68	0.91 : 1
<i>5</i>	17.3	76.56	0.93 : 1
<i>6</i>	17.03	65.67	1.06 : 1

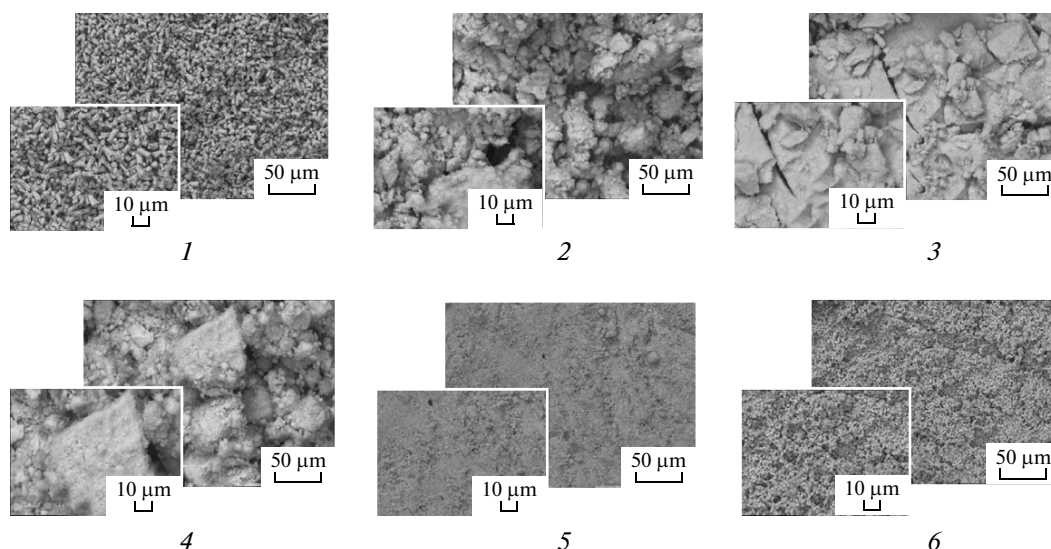
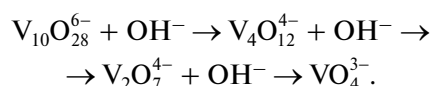


Fig. 1. Electron-microscopic images of samples 1–6 of bismuth orthovanadate.

impurities, which color the pigment brown-red. Alkalinization of the vanadate solutions causes the decavanadate ions to convert to a less condensed form. The decomposition of the decavanadate ion seems to involve the formation of intermediate vanadate ions with a lower degree of condensation:



To obtain a single-phase product, the pH of the suspension was raised from 0.6 to 3.5 by a 30% sodium hydroxide solution. As a result, the crystalline precipitate was observed to convert to loose amorphous substance (Figs. 1, 2, sample 2). The V : Bi molar ratio in the resultant product was 0.88 : 1 (Table 2), which was probably due to intensification of the bismuth salt hydrolysis process and incorporation of the poorly soluble hydrolysis products into the BiVO_4 precipitate. In the product obtained in this step, the particle size of the major phase (61.72%) ranges from 20 to 50 μm (Table 1).

In step 3, the stirring of the suspension for 1 h at room temperature leads to the aggregation of nuclei and formation of a denser amorphous precipitate (Figs. 1, 2, sample 3). The maximum particle size increases to 100 μm (Table 1). As seen from Table 2, ripening of the particles is accompanied by an increase in the vanadium content of the precipitate, and the V : Bi molar ratio in the product is 1.04 : 1, which is probably due to the recrystallization of the basic bismuth salts and formation of bismuth orthovanadate.

The addition of a 1 N sodium hydroxide solution to the suspension and the associated increase in pH to 6 (step 4) lead to the formation of an additional amorphous phase, which is adsorbed in the form of a loose layer on the dense amorphous precipitate formed

before (Figs. 1, 2, sample 4). According to the present results, a sharp increase in the pH of the mixture leads to the formation of bismuthyl nitrate impurities and a pale yellow precipitate. As a result, the bismuth content of sample 4 increases (Table 2). To improve the quality and color of the pigment, it is reasonable to adjust its pH only gradually, over a period of 1 h. The total particle size range of the precipitate obtained in this step of synthesis is 9–60 μm , and the major size fraction (74.76%) is 20–50 μm (Table 1).

Subsequent boiling of the suspension (step 5) can be used to convert amorphous bismuth orthovanadate with the general formula $\text{BiVO}_4 \cdot n\text{H}_2\text{O}$ to crystalline BiVO_4 . Holding the resultant mixture (pH \approx 6) at its boiling point is favorable for the formation of a denser,

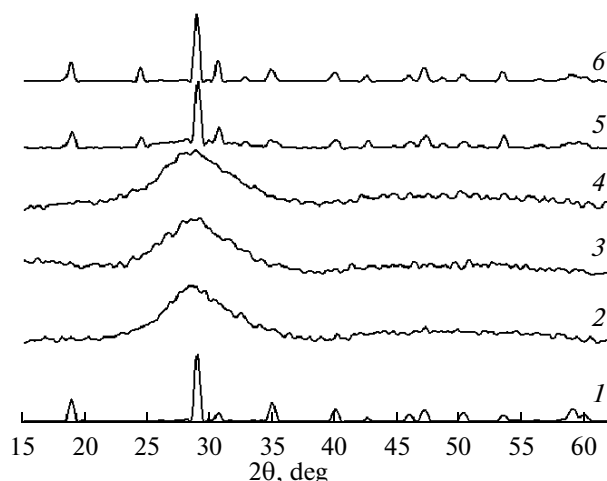


Fig. 2. X-ray diffraction patterns of samples 1–6 of bismuth orthovanadate.

Table 3. Lattice parameters, axial ratio (c/a), and unit-cell volume of bismuth orthovanadate samples

Sample	a , Å	c , Å	c/a	V , Å ³
1	5.150(1)	11.703(5)	2.272	310.5
5	5.140(3)	11.686(5)	2.273	308.9
6	5.155(2)	11.715(5)	2.272	311.4

fine bismuth orthovanadate powder (Figs. 1, 2, samples 5, 6). Increasing the heat treatment time of the suspension from 1.5 to 3 h increases the fraction of particles less than 5 μm in size from 7.62 to 30.83%, reduces the maximum particle size of the powders to 11 μm (Table 1), and increases the vanadium content of the forming material by 14% (Table 2).

According to X-ray diffraction data, the synthesized crystalline compound BiVO_4 (samples 1, 5, 6) has a tetragonal structure (Fig. 2). The unit-cell parameters of its body-centered tetragonal structure (Table 3) agree with data in the literature [7]. Our results indicate that the first step of synthesis (sample 2) leads to the formation of the clinobisvanite phase of bismuth orthovanadate. In step 5, boiling of the mixture for 1.5 h leads to a polymorphic transformation to the dreyerite phase of bismuth orthovanadate (sample 5). Increasing the heat treatment time increases the intensity of peaks in the X-ray diffraction pattern of the precipitate (sample 6) and its unit-cell volume (Fig. 2, Table 3).

The data in Table 1 indicate that the particles of the synthesized product (sample 6) are rather uniform in size: the major size fraction (56.91%) is 0.1 to 2.0 μm . As a rule, the use of pigments with such small particle sizes in the lacquer and paint coating industry allows one to significantly improve the performance parameters of finished products, such as intensity, brilliance, and spreading capacity [9].

Physicochemical characterization data for the synthesized pigment show that the true density of the powder, determined by the Archimedes method, is 6.72 g/cm³. The pH of the aqueous BiVO_4 suspension is 6, which ensures stability of a steel substrate in contact with the pigment.

The oil absorption value of the bismuth orthovanadate sample obtained is comparable to that of highly basic zinc chromates (30 g for 100 g of the pigment), which are dull yellow in color and have low intensity and lightfastness [1]. The oil absorption of kind II, which is defined as the amount of linseed oil needed to prepare ready-to-use paint (of appropriate consistency), is 56 g for 100 g of the pigment. The low oil absorption values of kinds I and II of bismuth ortho-

vanadate ensure a relatively low cost of paintwork materials based on it.

Studies of the chemical properties of the synthesized bismuth orthovanadate show that it is essentially insoluble in water and organic solvents but dissolves in highly alkaline (pH > 13) and acid (pH < 2) media. Our data demonstrate that coatings based on the synthesized pigment have good insulating properties.

CONCLUSIONS

We have proposed a technique for the solvothermal synthesis of bismuth orthovanadate using aqueous solutions of sodium vanadate and bismuth nitrate as precursors. The morphology of the synthesis products and their elemental and phase compositions were assessed in each step of synthesis. We obtained bright yellow powder whose particle size, morphological characteristics, and physicochemical properties meet the requirements for pigments in the lacquer and paint coating industry. The present results lead us to conclude that conventional chromium-containing pigments can be replaced by bismuth orthovanadate, a less toxic substance, in paintwork materials.

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SPELL: 1. DiffractPlus, 2. clinobisvanite, 3. dreyerite